ABSTRACT

DEPARTMENT OF CHEMISTRY

ALSHAHRANI, SAHAR S. B.S. KING KHALID UNIVERSTY, 2010

A THEORETICAL STUDY OF THE ELECTRONIC STRUCTURES OF TETRAHEDRAL BORON-HALOGEN COMPLEXES

Committee Chair: John H. Hall, Ph.D.

Thesis dated May 2019

This study addresses the structure and the bonding in the family of tetrahedral boranes. The specific molecules studied are the series B_4X_4 ($X = H, F, Br, Cl, I$), the series B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl and tetra-tert-butyl-tetraborane, t-Bu_4B_4.[12] The research presented herein employs the Hartree-Fock Self Consistent Field (HFSCF), the Moller-Plesset second order perturbation theory (MP2), and the Density Function Theory (DFT). A variety of basis sets was employed. Our calculations are the first theoretical studies of B_4Br_4, B_4I_4 B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl, and are also the first calculations for the D_{4h} structures of any of these molecules, except for B_4H_4. These results were compared with experimental results, where such comparisons can be made. The most energetically stable structure for all the B_4X_4 and $B_4Br_nCl_m$ molecules has symmetry T_d.

A THEORETICAL STUDY OF THE ELECTRONIC STRUCTURES OF TETRAHEDRAL BORON-HALOGEN COMPLEXES

A THESIS

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

BY

SAHAR SAEED ALSHAHRANI

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

MAY 2019

ACKNOWLEDGMENTS

First, I would like to thank God without whom nothing is possible. I would also like to express sincere thanks to my advisor, Dr. John Hall, for his guidance, inspiration, invaluable advice, and knowledge that contributed so greatly to this project. I am thankful for both committee members, Dr. Conrad Ingram and Dr. Dinadayalane Tandabany, for their comments and suggestions to make this thesis an excellent one. I would like to thank the Saudi Arabian Cultural Ministry and Clark Atlanta University for their financial support.

I am highly indebted and thoroughly grateful to my mother, Shakah Alshahrani, and my father, Saeed Alshahrani, for their love and encouragement. This thesis would not have been possible without them. I dedicate this thesis to my lovely sisters, Samer and Shmook. Also, it is a great pleasure to acknowledge my deepest gratitude to my brothers, Mohammed, Abdullah, and Abdullaziz. They have always encouraged me and given me good advice in everything I have done in my life. In addition, my thanks and appreciation go to my brothers and sisters. Finally, I am grateful to all of my friends for their support and for making this study enjoyable.

TABLE OF CONTENTS

CHAPTER

LIST OF FIGURES

Figure

LIST OF TABLES

Table

Table

CHAPTER 1

INTRODUCTION

The purpose of this study was to gain insight into the bonding in the family of highly symmetrical tetrahedral borane compounds. This family of compounds presented a unique opportunity to gain a deeper understanding of chemical bonding in all molecules. Atoms, such as boron, where there are more valence orbitals than valence electrons are electron deficient. Electron deficient atoms typically form three-center bonds, as well as single bonds with other atoms or atom groups, resulting in highly symmetrical tetrahedral, icosahedral, and dodecahedral geometries. Back bonding from the hydrogen to the boron cage was originally used to explain the stability of this family of molecules. However, the synthesis of tetra-tert-butyl-tetraborane, t-Bu_4B_4[1] showed that extensive back-bonding is not required for stability in the B_4X_4 molecules. The molecules $B_4Br_2Cl_2$, B_4Br_3Cl, B_4Br_4, B_4Cl_4, and B_4Br_4 are stable and have been chemically characterized.[2]

There have been several theoretical studies of B_4Cl_4. The first was by Hall and Lipscomb.[3] The species B_4F_4 and B_4H_4 are have not been experimentally observed. While B_4Br_4, was synthesized by Ahmed and Morrison in 1992[2] and has been the subject of several theoretical studies, little experimental characterization has been achieved. The molecules B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl have been synthesized and

characterized by NMR spectroscopy. Our theoretical studies are the first for these systems.

1.1 The B_4H_4 Molecule and its Halogen Derivatives

1.1.1 B_4H_4

The initial ab initio Hartree-Fock Self-Consistent-Field study of hypothetical B_4H_4, by Epstein and Lipscomb, employed a tetrahedral geometry, as in B_4Cl_4.[5,6] Many studies of B_4H_4 were subsequently performed in an effort to resolve questions around its geometry.[4,7] Perhaps the most comprehensive and accurate treatment was by McKee and Lipscomb.[1] These authors performed extensive potential energy surface calculations and concluded that the most stable structure for B_4H_4 is tetrahedral, although D_{2h} structure was proposed as an intermediate structure between the T_d and the higher energy D_{4h} structures. Several recent studies suggest that a C_s structure were more stable than a tetrahedral structure.[8,9]

1.1.2 B_4F_4

Kleier et al. studied the degenerate rearrangement of tetrahedral B_4H_4 and B_4F_4 through a planar D_{4h} midpoint structure. The T_d structure was energetically favoured in all calculations.[10]

1.1.3 B_4Cl_4

Tetraboron tetrachloride, B_4Cl_4, was first synthesized by glow discharge of BCl_3 using Hg electrodes and then later by the spontaneous decomposition of tetrachlordiborane B_2Cl_4.[5,11] B_4Cl_4 is a yellow solid that melts at 95 °C and decompose at

125 °C.[12] The structure of B_4Cl_4 was predicted to be T_d with all boron atoms being equivalent, just from a simple stoichiometric calculations of B_4Cl_4 reaction with methanol.[14] The crystal structure of B_4Cl_4 was determined by Atoji and Lipscomb[6] to be tetrahedral. The measured B–Cl bond length was 1.69 Å and the B–B distance was approximately 1.7 Å. The IR spectrum was measured by Brown et al.[13] and consisted of a single absorption at 968 cm^{-1}. The T_d structure of the B_4Cl_4 molecule was reconfirmed by He(I) photoelectron spectra,[18] electron diffraction study,[19] infrared spectra,[20] and theoretical studies.[1,3,14]

1.1.4 B_4Br_4

Bromine (Br) substituted derivatives of B_4H_4 were synthesized and identified using ^{11}B NMR by Morrison.[2,12] The B_4Br_4 molecule, along with B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl, were produced from the reaction of B_4Cl_4 with BBr_3 in the presence of $AlBr_3$.[2] The authors also discovered that the reaction of B_4Br_4 with BCl_3 is very efficient and regenerates B_4Cl_4. These compounds are identified using the chemical shifts from the ^{11}B NMR spectra, which show two resonances for the B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl compounds, indicating T_d structure.[2] The small ^{11}B – ^{11}B coupling constant of these compounds points to the existence of the B–B–B multicenter bonds. It was also postulated that B_4F_4 and B_4I_4 could also be synthesized using similar reaction pathways.[2]

Another area of theoretical studies is focused on the relative stabilities of the tetrahedral and planar isomers of B_4H_4, B_4F_4, and B_4Cl_4 .[1,4,12] In early studies, the T_d structure of all these compounds was calculated to be more stable than the planar D_{4h} structure. Studies of the isomerization from the T_d to D_{4h} structure revealed large barrier

due to orbital crossing.[10] In the T_d isomers of these compounds there are significantly large electron densities in the middle of the each face of tetrahedron, which is the result of the B–B–B three center one electron bond.[3] These faces can act as a hydrogen bond donor to form complexes with acids like HCl.[16]

Therefore, the study perform calculations on the B_4H_4 molecule, and on its halogen derivatives to compare energetic differences between tetrahedral (T_d) and planar structures, employing three different methods (HF, MP2, and DFT) combined with a series of basis sets of increasing order. Our systematic study will give unambiguous ordering of isomer stability that is free from method or basis set bias. Besides that, our calculations represent the first density functional study of gas phase B_4I_4, B_4Br_4 molecules, and the first correct electronic structure calculations on B_4Cl_4.

CHAPTER 2

COMPUTATIONAL METHODS

2.1. The Hartree Fock (HF) Method

The Hartree-Fock (HF) method is the basic ab-initio model for quantum mechanical calculations for atoms and molecules. The HF theory is fundamental to the electronic structure theory because the equations are relatively simple, yet capable of describing profound chemical structures. In the HF theory, the Hamiltonian consists of electron kinetic energy, electrostatic potential energy of electrons and nucleus, and the exchange energy that results from the Pauli exclusion principle. The Hamiltonian in HF theory ignores one term of correlation energy.[17,18] The method used in the current research is based on quantitative theory principles and has been developed and improved by many scientists and researchers. In 1928, the English scientist, Glass Hartree, was able to develop the first quantitative model for multi-electron atoms. In 1930, Vladimir Fock made a breakthrough and updated Hartree's theory to include electron rotations. The self-consistent field method is used to find the approximate wave functions as well as the energy levels in the atoms of several electrons. Considering the principle of Pauli exclusion, the primary wave functions can be considered as hydrogen atoms, and numerical equations can be solved by using the computer. The results of the Hartree-Fock

theory are valid enough to show that the electron density is in envelops around the atoms and can be used quantitatively to show the chemical cycle. [19]

The HF theory is fundamental to the electronic structure theory because the equations are relatively simple, yet capable of describing profound chemical structures. In the HF theory, the Hamiltonian consists of electron kinetic energy, electrostatic potential energy of electrons and nucleus, and the exchange energy that results from the Pauli Exclusion Principle. In addition, the HF theory Hamiltonian ignores one term in the, the correlation energy.

2.2. The Møller-Plesset Perturbation Theory

The HF theory assumes a single Slater determinant wavefunction appropriate for non-interacting particles, resulting in an averaged, effective single-particle treatment neglecting electron correlation. One way to account for electron correlation is to correct the HF results posteriori, treating electron correlation as a perturbation. Perturbation theory [20] is based upon dividing the Hamiltonian into two parts, a reference $\hat{H}_0$, and a perturbation $\hat{H}'$

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

where $\hat{H}_0$ is an exactly solvable Hamiltonian, λ is a parameter formally controlling the size of the perturbation, and the $\hat{H}'$ term is the perturbation.

The question, however, comes in the cases where the Hamiltonian cannot be divided to a reference $\hat{H}_0$ and a perturbation $\hat{H}'$. In this case, one of the two methods is usually used: The variation method is particularly useful in estimating the energy values of the stable state and the first few activated states of the system, and gives an idea of its

wavefunctions. The other method, the Wentzel, Kramers, and Brillouin (WKB) method, is useful in finding the characteristics of the energy and the wavefunctions of the systems where classical boundaries are applied.[21]

Furthermore, the method of perturbation, the variation and WKB methods do not require the presence of a precisely identifiable Hamiltonian. The application of the approximation methods in the study of stable states consists of finding the characteristic values of the energy and wave functions that are non-time-dependent Hamiltonian, as they have no exact solutions.

2.3. The Density Functional Theory

2.3.1 The Theory

Density Functional Theory is a quantum mechanical (QM) method that can be employed in diverse research fields including physics, chemistry and materials science. Density Functional Theory methods are often used to study the ground state electronic structure of multi-particle systems like atoms and molecules, among others.[22] DFT has been established as a valuable research tool because it can serve either to validate the conclusions that have been reached from the analysis of the experiments or to distinguish between those possibilities that were left open. The calculation of a wide range of molecular properties with DFT allows a close connection between theory and experiment and often leads to important clues about the geometric, electronic, and spectroscopic properties of the systems being studied.

Density Functional Theory attempts to address both the inaccuracy of HF and the high computational demands of post-HF methods by replacing the many-body electronic

wavefunction with the electronic density as the basic quantity, whereas the wavefunction of an N electron system is dependent on 3N variables (three spatial variables for each of the N electrons), the density is a function of only three variables and is a simpler quantity to deal with both conceptually and practically, while electron correlation is included in an indirect way from the outset. Walter Kohn and Pierre Hohenberg laid strong theoretical foundation for DFT in the framework of the two Hohenberg-Kohn (H-K) theorems.[23] The first H-K theorem demonstrates that "the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates." The second theorem defines energy functional for the system and proves that the correct ground state electron density minimizes this energy functional. Thus, the problem of solving the many-body Schrödinger equation is bypassed, and now the objective becomes to minimize a density functional. Note, however, that although the H-K theorems ensure that the density functional is a universal quantity they do not specify its form.

Three different types of approximations involved in DFT are: Local functionals (e.g., LDA - Local Density Approximation); Semi-local or Gradient-dependent functionals (e.g., GGA - Generalized Gradient Approximation); and Orbital functionals and other nonlocal approximations (e.g., hybrids and Meta-GGA).[22] LDA methods are based on the theory that the surface of the molecule possesses equal density throughout. It is known that the LDA approximates the energy of the true density by the energy of a local constant density. LDA fails when the density undergoes rapid changes such as in molecules. GGA considers the gradient of the electron density. The incorporation of

some of the features from ab initio methods, like HF method, and a few of the other more refined features of DFT mathematics are used by hybrid methods. One of the most popular examples of hybrid methods is B3LYP.[24] In the past decade, several DFT functionals have been developed and some of them become very popular in a short period of time (e.g., M06 functionals, ωB97XD and B3PLYP). Certain DFT methods are also created keeping in mind a definite purpose. For example, the MPW1K hybrid method was created for calculations involving kinetic studies. Because it is reliable and computationally inexpensiveness, DFT has been regarded as potentially the most successful and followed approaches with regards to quantum mechanics.[25,26]

Density Function Theory calculations can be employed to understand the structures, electronic and vibrational properties of molecules. They are often used to find the binding energy of molecules involved in non-bonding interactions and the band structure of solids. However, there is a growing interest to apply quantum chemical calculations, in particular, DFT calculations in the fields of biology and mineralogy that are not closely associated with quantum mechanics. Computations employing DFT methods are helpful to assist experimental investigations in characterizing the compounds, validating the reaction mechanisms.[22,26]

One of the benefits of DFT methods is the enhancement in computational accuracy without the overhead of increasing the computing time. However, DFT methods also have a few drawbacks. For instance, they can pose difficulties in describing intermolecular interactions like van der Waals forces, charge transfer excitations, and calculations of band gap and ferromagnetism in semiconductors.[22,26]

2.3.2 The B3LYP Functional

Becke three parameter exchange and Lee-Yang-Parr correlation functional (B3LYP) has been considered as the most popular hybrid functional until last decade for a variety of reasons.[24,27] It exhibited a remarkable improvement over HF method in terms of computation times. It has also been regarded as relatively robust as compared to other models. Computation of the exchange part of the XC energy (exchange-correlation energy, which is the difference between the exact total energy of a system and the classical Hartree energy) is carried out from the electronic wave functions. This is subsequently mixed into LDA or GGA energy. However, the precise ratio used in this mixture has not been determined.

The new parameterization of the B3LYP functional came into being after it was found that one of the factors that splitting of energy relies on is the exact exchange admixture parameter. Development of B3LYP functional persuaded computational chemists to use DFT in predicting physicochemical properties of molecules and reaction barriers.[22,25] The significance of B3LYP functional can be reflected by the fact that it was used as the basis for designing other hybrid exchange correlation functionals. Many scientists and researchers have used B3LYP as their default functional because it has stood as a benchmark for numerous systems. This is supplemented by the fact that B3LYP's performance is far superior as compared to some of the other density functionals. Some of the errors in non-empirical functionals are seen having a systematic pattern. For example, the PBE functional which belongs to the generalized gradient approximation functional for exchange correlation energy that overestimates bonding

distances and, on the contrary, underestimates vibrational frequencies. Estimating the target property, as a result, becomes significantly easy. Furthermore, using these functionals can result in increased accuracy in relative quantities like, but not limited to, energy differences, frequency shifts and changes in bond length. Such properties can also be noted in functionals like B3LYP, which is principally due to significant error cancellation. Nevertheless, B3LYP also presents a drawback with regards to attaining lesser accuracy for larger molecules.

2.4. Calculation

Our focus on this study is the total energy of B_4X_4 molecules for planar and tetrahedral geometries, where the X = H, Cl, F, Br, I. The goal is to compare the stabilities of planar and tetrahedral geometry of the same compound, and also want to discern trend within the B_4X_4 molecular family. In order to avoid disadvantages of certain methods, HF, MP2, and DFT methods were employed to calculate various properties of the above-mentioned molecules using basis sets of increasing complexity. The basis sets that were employed are all Gaussian type, and they are 6-31G*, 6-311G*, 6-311+G** for the HF method. The basis sets used for the MP2, and DFT methods are similarly of Gaussian type. The Spartan16 software was used for all calculations.[2]

CHAPTER 3

RESULTS AND DISCUSSION

3.1 The Stability of the D_{4h} and T_d Isomers

Calculations were performed on the D_{4h} and T_d structures of the B_4X_4 (where X = H, F, Cl, Br, I) molecular series employing HF, MP2, and B3LYP/DFT theory using Gaussian type basis sets of increasing basis functions. First, the results of all calculations are presented in tables.

It is clear from Table 1, Table 2, and Figure 1 that the tetrahedral T_d isomer is more stable than the planar D_{4h} isomer for all molecules at all levels, when the 6-31G* basis set is used. The T_d isomers of the molecules B_4X_4 (X=H, F, Cl, Br) are much more stable at the HF level than at the MP2 and DFT level, and the stability of the T_d isomer at the latter two levels are comparable.

Table 1. Calculated Energies (Hartree) of the D_{4h} and T_d Geometry, for the B_4X_4 (X=H, F, Cl, Br) Molecules at HF, MP2, and B3LYP/DFT Theory with 6-31G* Basis Set

		Molecules			
Methods	**Energetics**	B_4H_4	B_4F_4	B_4Cl_4	B_4Br_4
HF	$E(D_{4h})$	-100.72920	-496.49490	-1936.60910	-10387.05420
	$E(T_d)$	-100.92570	-496.61770	-1936.74600	-10387.16860
MP2	$E(D_{4h})$	-101.10550	-497.55310	-1937.52450	-10387.92170
	$E(T_d)$	-101.27140	-497.64460	-1937.62240	-10387.98640
DFT	$E(D_{4h})$	-101.57220	-498.84090	-1940.22720	-10394.92050
	$E(T_d)$	-101.71280	-498.93530	-1940.31540	-10394.99070

Table 2. The Energy Differences ΔE (kcal/mol) between D_{4h} and T_d Geometries

Methods	Energetics	Molecules			
		B_4H_4	B_4F_4	B_4Cl_4	B_4Br_4
HF	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	123	77	86	72
MP2	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	104	57	61	41
DFT	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	88	59	55	44

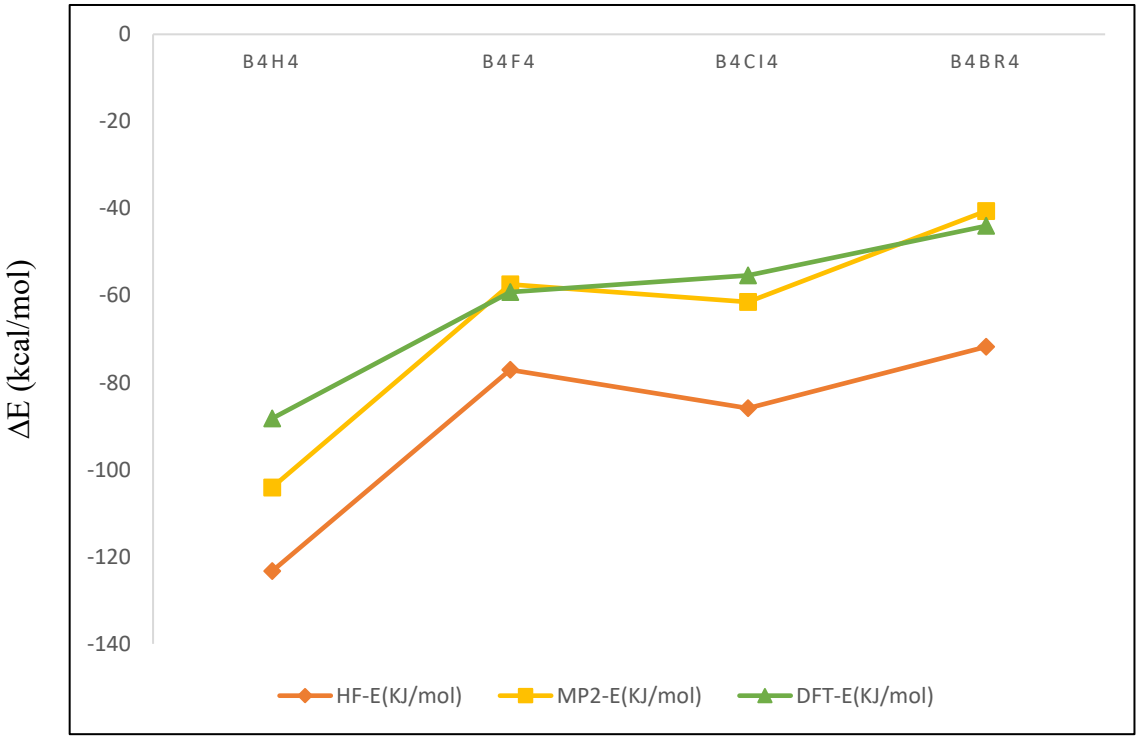

Figure 1. The energy differences ΔE (kcal/mol) between the **D_{4h}** and **T_d** geometries of the various molecules, calculated at the HF, MP2, and B3LYP/DFT level with 6-31G* basis sets.

The comparison of the stability of the T_d isomer at different level of theory is shown in Table 3. Previous studies[4,10] on the B_4F_4 and B_4Cl_4 molecules calculated smaller stability of the T_d isomer compared to the planar D_{4h} isomer, ~25 kcal/mol or smaller whereas our calculations shows much larger stabilization of ~80 kcal/mol. The reason of differences can be explained as a result of the smaller basis sets used in earlier studies and the results of these studies can be interpreted only qualitatively.

Table 3. The Stability Order of the $\mathbf{T_d}$ Isomers Calculated Using the 6-31G* Basis Set and at Different Levels of Theories

Molecules	Stability order of the T_d isomer
$\mathbf{B_4H_4}$	HF>MP2> DFT
$\mathbf{B_4F_4}$	HF>DFT>MP2
$\mathbf{B_4Cl_4}$	HF>MP2> DFT
$\mathbf{B_4Br_4}$	HF>DFT>MP2

Shown in Tables 4 and 5 are the energies of the D_{4h} and T_d isomers and their differences calculated using the 6-311G* basis set at various levels of theory. At all levels and for all the molecules considered here, the T_d isomer is more stable than the D_{4h} isomer (see Figure 2), which is consistent with results of the findings obtained when the smaller 6-31G* basis set is used.

Table 4. Calculated Energies (Hartree) of the D_{4h} and T_d Geometries, for the B_4X_4 (X=H, F, Cl, Br, I) Molecules at HF, MP2, and B3LYP/DFT Theory with 6-311G* Basis Set

Methods	Energetics	Molecules				
		B_4H_4	B_4F_4	B_4Cl_4	B_4Br_4	B_4I_4
HF	$E(D_{4h})$	-100.745282	-496.623476	-1936.72691	-10388.12650	-27765.88350
	$E(T_d)$	-100.940931	-496.746787	-1936.86298	-10388.24120	-27766.03930
MP2	$E(D_{4h})$	-101.139197	-497.83635	-1937.69557	-10389.05080	-27766.74090
	$E(T_d)$	-101.300814	-497.92518	-1937.78873	-10389.11050	-27766.84150
DFT	$E(D_{4h})$	-101.58931	-498.99222	-1940.34632	-10395.98720	-27777.48570
	$E(T_d)$	-101.728033	-499.08252	-1940.44463	-10396.05530	-27777.58060

Table 5. The Energy Differences ΔE (kcal/mol) between D_{4h} and T_d Geometries

Methods	Energetics	Molecules				
		B_4H_4	B_4F_4	B_4Cl_4	B_4Br_4	B_4I_4
HF	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	123	77	85	72	98
MP2	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	101	56	58	37	63
DFT	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	87	57	62	43	60

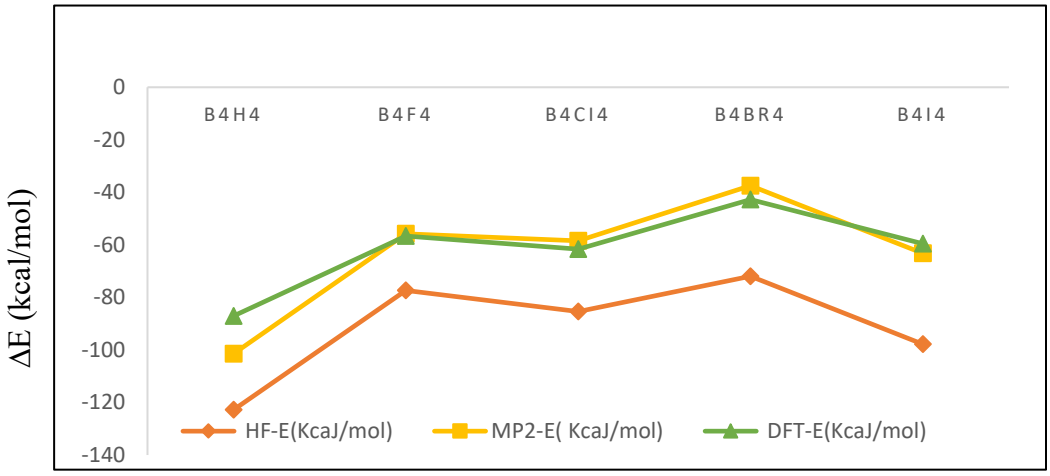

Figure 2. The energy differences ΔE (kcal/mol) between the $\mathbf{D_{4h}}$ and $\mathbf{T_d}$ isomers of the various molecules, calculated at the HF, MP2, and B3LYP/DFT level with 6-311G* basis set.

The tetrahedral isomers T_d are more stable at the HF level than at the MP2 and B3LYP/DFT levels, at least by 20 kcal/mol. The stability of the T_d isomers compared to the D_{4h} isomers of each molecule at the MP2 and B3LYP/DFT levels are similar (see Table 6).

Table 6. The Stability Order of the $\mathbf{T_d}$ Isomers Calculated Using 6-311G* Basis Set and at Different Levels of Theories

Molecules	Stability order of the T_d isomer
$\mathbf{B_4H_4}$	HF>MP2> DFT
$\mathbf{B_4F_4}$	HF>DFT>MP2
$\mathbf{B_4Cl_4}$	HF > DFT>MP2
$\mathbf{B_4Br_4}$	HF>DFT>MP2
$\mathbf{B_4I_4}$	HF>MP2> DFT

The largest basis set that were used is 6-311+G** which includes diffusion type sp functions and polarization functions on all atoms. The results of the energy calculations at various levels using the 6-311+G** basis set is listed in Table 7. Again, consistent with the results obtained using the smaller basis sets 6-31G* and 6-311G*, the tetrahedral T_d isomers of all molecules are more stable than the planar D_{4h} isomers, at all three levels of theory employed here.

Table 7. Calculated Energies (Hartree) of the $D_{4h}$and T_d Geometries, for the B_4X_4 (X=H, F, Cl, Br, I) Molecules at HF, MP2, and B3LYP/DFT Theory with 6-311+G** Basis Set

Methods	Energetics	Molecules				
		B_4H_4	B_4F_4	B_4Cl_4	B_4Br_4	B_4I_4
HF	$E(D_{4h})$	-100.75183	-496.63416	-1936.82560	-10388.12780	-27765.88470
	$E(T_d)$	-100.94813	-496.75651	-1936.87015	-10388.24300	-27766.04020
MP2	$E(D_{4h})$	-101.17080	-497.85430	-1937.68300	-10389.06000	-27766.75000
	$E(T_d)$	-101.33100	-497.94140	-1937.79900	-10389.12000	-27766.85000
DFT	$E(D_{4h})$	-101.59510	-499.00410	-1940.35200	-10395.99000	-27777.49000
	$E(T_d)$	-101.73470	-499.09360	-1940.4500	-10396.06000	-27777.58000

The T_d isomer of the B_4H_4, B_4F_4, B_4Br_4, and B_4I_4 molecules at the HF level are more stable than at the MP2 and B3LYP/DFT levels, consistent with previous results. However, the T_d isomer of the B_4Cl_4 molecule is more stable than the D_{4h} isomer only by 28 kcal/mol, which is far small than the results of 85 kcal/mol of the 6-311G* basis set, and smaller than the stability calculated at the MP2 and B3LYP/DFT levels (see Table 8, Table 9, and Figure 3).

Table 8. The Energy Differences ΔE (kcal/mol) between D_{4h} and T_d Geometries

Methods	Energetics	Molecules				
		B_4H_4	B_4F_4	B_4Cl_4	B_4Br_4	B_4I_4
HF	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	123	77	28	72	98
MP2	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	101	55	73	38	63
DFT	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	88	56	62	43	59

Table 9. The Stability Order of the $\mathbf{T_d}$ Isomers Calculated Using 6-311+G* Basis Set and at Different Levels of Theories

Molecules	Stability Order of the T_d Isomer
$\mathbf{B_4H_4}$	HF>MP2> DFT
$\mathbf{B_4F_4}$	HF>DFT>MP2
$\mathbf{B_4Cl_4}$	MP2> DFT>HF
$\mathbf{B_4Br_4}$	HF>DFT>MP2
$\mathbf{B_4I_4}$	HF>MP2> DFT

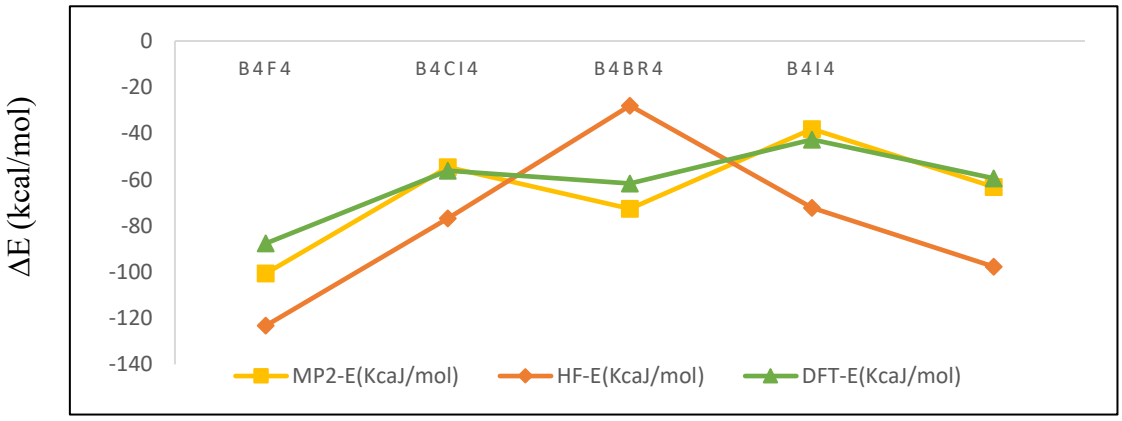

Figure 3. The energy differences ΔE (kcal/mol) between $\mathbf{D_{4h}}$ and $\mathbf{T_d}$ isomers of the various molecules, calculated at the HF, MP2, and B3LYP/DFT level with 6-311+G** basis set.

The decreased stability of the T_d isomer at the HF level when the largest basis set 6-311+G** used is surprising and anomalous to the trends observed when the basis sets are enlarged from 6-31G* to 6-311G*, and also an outlier when compared the trend in other molecules. In order to find the reason of this anomaly, will plot the basis set dependence of B_4Cl_4 energy, as shown in Figure 4. It is clear from the Figure 4 that at the MP2 and B3LYP/DFT levels the energy does not change considerable when basis set is increased to 6-311+G** from 6-311G*, i.e. the basis set is converged. The same is true for the $T_d$isomer at the HF level. However, the planar D_{4h} isomer energy is substantially decreased upon basis set increase, and show almost linear trend. Although the basis set is converged for the D_{4h} isomer at the HF level, a larger basis set should be employed to get accurate results.

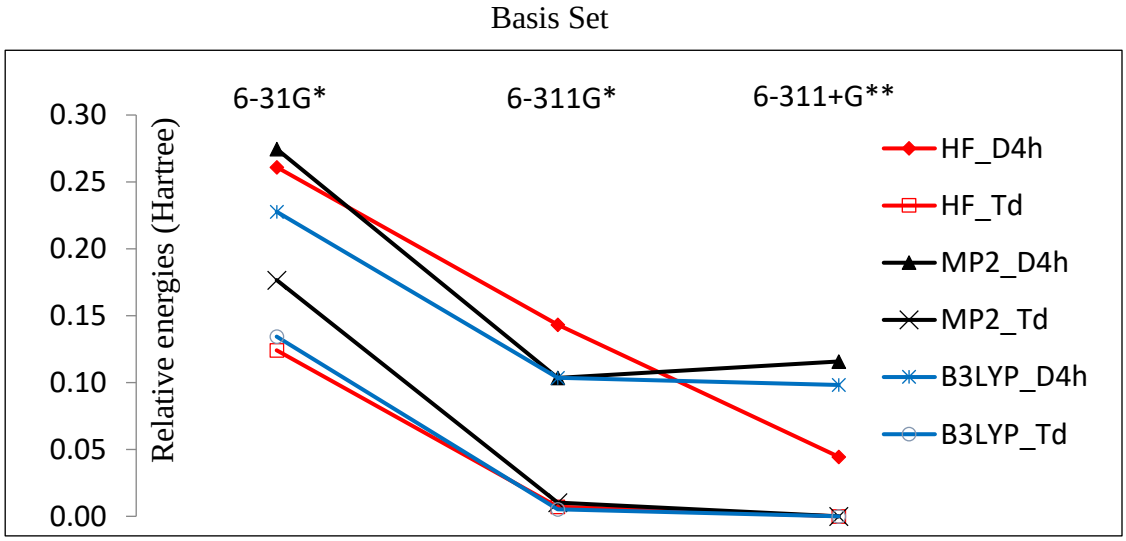

Figure 4. Relative energies (Hartree) of the $\mathbf{B_4Cl_4}$ molecule at the $\mathbf{D_{4h}}$ and $\mathbf{T_d}$ geometry, calculated at the HF, MP2, and B3LYP/DFT level with various basis sets, as indicated.

(The relative energy is with respect to the lowest energy of the $\mathbf{T_d}$ form at each level, calculated using the 6-311+G** basis set, which is -1936.87014 for HF, -1937.79905 for MP2, and -1940.44978 Hartree for the B3LYP/DFT level of theory.)

In Table 10, the atomic total energy and eigenvalues were calculated for the Cl atom at HF level, resulting in the eigenvalue of Cl is 0.50288 at HF level which much close to NIST result by 5.73%. Therefore, there is no error in B_4Cl_4 calculation at HF with 6-311+G** and the basis set is converged.

Table 10. Atomic Total Energy and Eigenvalues for the Cl Atom

	IP CL	**E_{tol}**	**Eigenvalues**	**E_{xptl}**
Calculation	11.27	-460.94233	0.50288	5.73%
NIST Calculation	12.93	-458.66400	0.47564	

3.2 Basis Set Dependence

In the previous section, the results of all calculations on the D_{4h} and T_d structures of the B_4X_4 (where X = H, F, Cl, Br, I) molecular series were discussed. In this section, the discussion is about the effect of basis sets on the calculated energy, using B_4H_4 and B_4Br_4 as examples. Then all results are tabulated and the findings are discussed.

The basis sets that were used here are 6-31G*, 6-311G*, and 6-311+G**. All these basis sets are split valence type; the 6-31G* basis set represents inner shells by one contracted Gaussian, and valence shell by two contracted Gaussian, and the contracted Gaussians are obtained by linear combination of a number of primitive Gaussian functions, as indicated in each basis set. The '*' represents addition of polarization functions (d type) to all atoms except H atom, and '**' denotes addition of polarization functions (p type) on H atom as well.[29,30] The 6-311G* basis set is of triple zeta (TZ) quality, i.e. it represents the outer valence shells using 3 contracted Gaussian functions, whereas the 6-31G* basis sets use only two. The 6-311G* basis set is expected to give

better results when compared to the double zeta (DZ) quality basis sets, because in it the valence electrons are more flexible.[31,32] The next level of basis set is 6-311+G** which includes diffuse functions{denoted by (+)} and polarization functions on all atoms.[32]

Figure 5 shows the energy difference (ΔE) between the T_d and D_{4h} isomer of the B_4H_4 molecule calculated at the HF, MP2, and B3LYP/DFT level of theory employing various basis sets. At the HF and DFT level, the calculated ΔE are ~123 kcal/mol and ~88 kcal/mol, respectively, and both do not show strong basis set dependence. At the MP2 level, on the other hand, ΔE shows noticeable but small basis set dependence; ΔE calculated using the 6-31G* basis set is ~104 kcal/mol, and ΔE decreases as the basis set becomes more complete, and its value is ~101 kcal/mol when the 6-311+G** basis sets is employed.

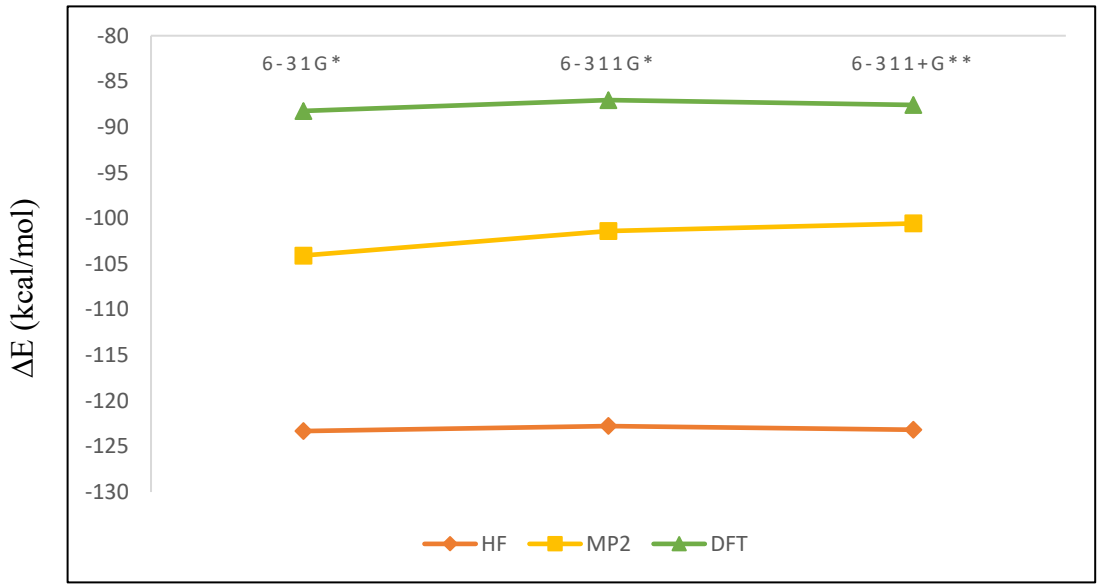

Figure 5. The energy differences ΔE (kcal/mol) between the $\mathbf{D_{4h}}$ and $\mathbf{T_d}$ geometry of the B_4H_4 molecule, calculated at the HF, MP2, and B3LYP/DFT level with various basis sets, as indicated.

It also worth noting that the calculated ΔE is largest at the HF level, smallest at the B3LYP/DFT level, and the value is in between when MP2 level of theory are used. These ranking does not show dependence on the basis set. The ranking is also consistent with fact that in HF electron correlation was completely ignored, and MP2 takes electron correlation into account in some degree, and at the DFT level electron correlation is explicitly considered.[33] The calculated energy difference using the 6-31G* basis set here is -123 kcal/mol at the HF level and -104 kcal/mol at the MP2 level. These values are larger than the results of previous studies[1,4,10] of ~76 kcal/mol, presumably due to the small basis sets were employed in the early studies.

Since the Br atom is larger than H atom and has more electrons, it is expected that the energy should show stronger basis set dependence in B_4Br_4 than in B_4H_4. When the basis set is increased from 6-31G* to 6-311G*, the energy decrease in the B_4H_4 molecule is less than one tenth of Hartree; however in the B_4Br_4 molecule, the decrease is about one Hartree at all three levels of theory. When comparing the absolute value of energy, the B3LYP/DFT energy is much smaller than MP2 energy, which is slightly smaller than the HF energy at all basis sets, irrespective of isomer D_{4h} or T_d. It is clear from Figure 6 that increasing basis set from 6-311G* to 6-311+G* does not improve the results much. The energy difference ΔE between the D_{4h} and T_d isomers of the B_4Br_4 molecule is largest at the HF level, and at the DFT and MP2 level, it is comparable. The trend is slightly different when compared to the trend in the B_4H_4 molecule, where ΔE values at the MP2 are larger than the values calculated at the DFT level, and are notably different.

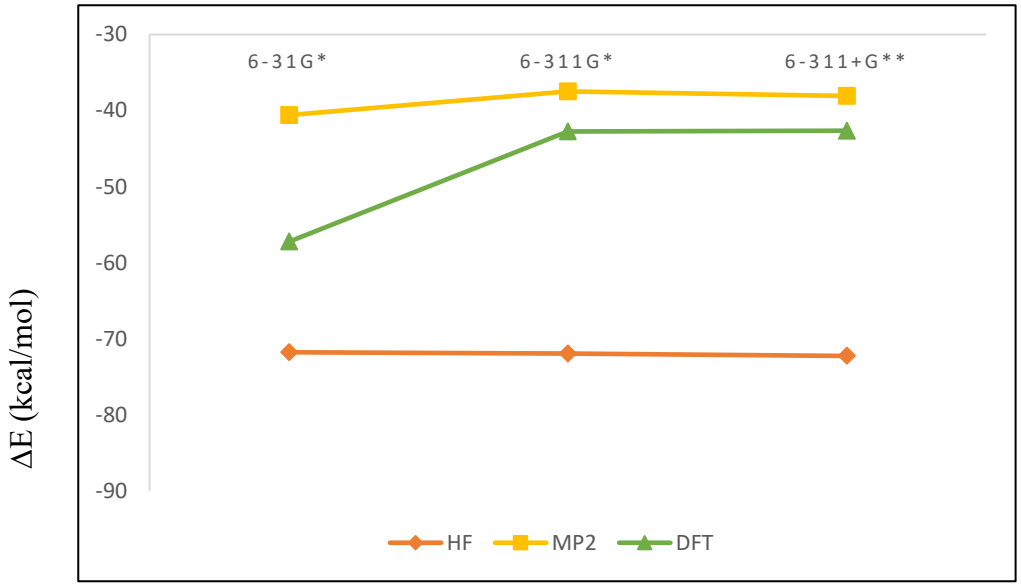

Figure 6. The energy differences ΔE (kcal/mol) between the $\mathbf{D_{4h}}$ and $\mathbf{T_d}$ geometry of the $\mathbf{B_4Br_4}$ molecule, calculated at the HF, MP2, and B3LYP/DFT level with various basis sets, as indicated.

Both the molecule series $B_4Br_nCl_m$ (n+m=4 and n≠0,m≠0) and calculated the energy differences between the tetrahedral isomers and the planar D_{4h} isomers at the B3LYP/6-311+G** level were considered. Morrison et al.[2,12] synthesized these compounds and experimentally characterized, so our motivation is to get some insight about the stabilities of these compounds by comparing the experimental and theoretical results. the B3LYP/6-311+G** level is the chosen level to optimize the geometry, and calculate the energy and the harmonic vibrational spectra because the combination of the method with the basis set seems to give reasonably accurate results for the B_4X_4 (X=H, F, Cl, Br, I) series of compounds that presented earlier. The results are presented in Table 11, and the energy differences between the T_d isomers and the D_{4h} isomers are shown in Table 12.

Table 11. Calculated Energies (Hartree) of the D_{4h} and T_d Geometry, for the $B_4Br_nCl_m$ (n+m=4 and n≠0,m≠0) Molecules at B3LYP/DFT Theory with Various Basis Sets

Basis Set	Energetics	Molecules		
		B_4BrCl_3	$B_4Br_2Cl_2$	B_4Br_3Cl
6-31G*	$E(D_{4h})$	-4053.90404	-6167.58578	-8281.26756
	$E(T_d)$	-4053.99561	-6167.67589	-8281.35614
6-311G*	$E(D_{4h})$	-4054.26105	-6168.17570	-8282.09039
	$E(T_d)$	-4054.35862	-6168.27267	-8282.18668
6-311+G**	$E(D_{4h})$	-4054.26542	-6168.17915	-8282.09292
	$E(T_d)$	-4054.36281	-6168.27592	-8282.18900

Table 12. The Energy Differences ΔE (kcal/mol) between D_{4h} and T_d Geometry

Basis set	Energetics	Molecules		
		B_4BrCl_3	$B_4Br_2Cl_2$	B_4Br_3Cl
6-31G*	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	57	70	56
6-311G*	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	61	74	60
6-311+G*	$E(T_d)$-$E(D_{4h})$ (kcal/mol)	61	60	60

The energies of all the molecules decrease to ~ one half of Hartree when the basis set increased from 6-31G* to 6-311G*, and decrease is smaller than one tenth of Hartree when basis set is further increased to 6-311+G**. This is a clear indication of basis set convergence for these molecules. The energy differences between the T_d isomers and the D_{4h} isomers does show significant basis set dependence, as shown in Figure 7.

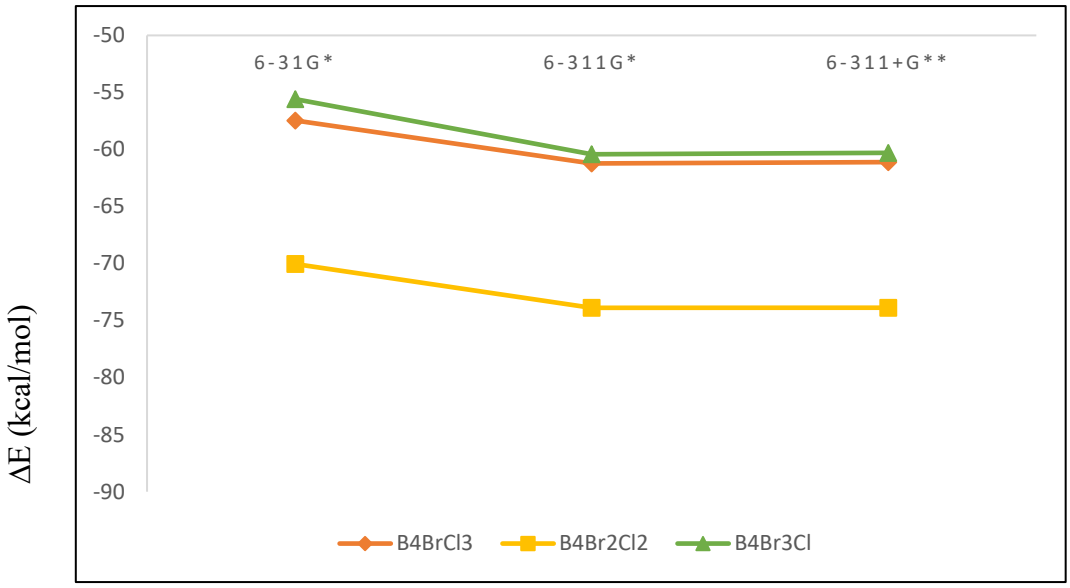

Figure 7. The energy differences ΔE (kcal/mol) between the $\mathbf{D_{4h}}$ and $\mathbf{T_d}$ isomers of the various $B_4Br_nCl_m$ (n+m=4 and n≠0,m≠0) molecules, calculated at the B3LYP/DFT level with various basis sets, as indicated.

It is reported by Papakondylis and Mavridis for the first time that the global minimum structure of B_4H_4 is planar with C_s symmetry (C_s (I) in Figure 8.[7] Further high level calculations confirmed that the planar structure, C_s(I) , is indeed the most stable structure.[8,9]

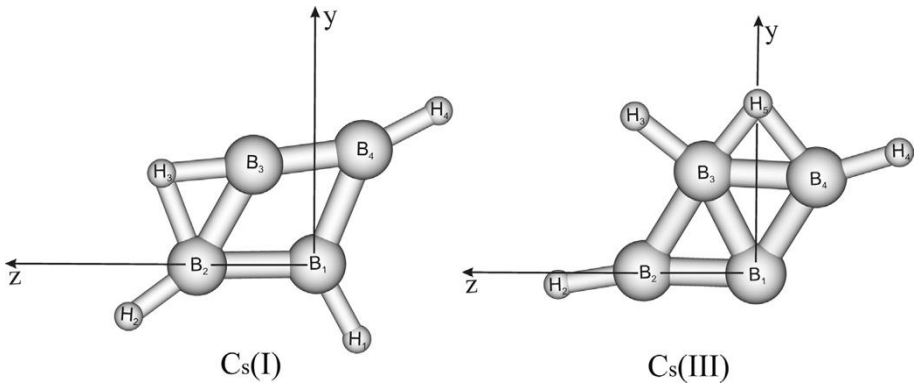

Figure 8. Planar structures of B_4H_4. The C_s (I) is the most stable structure of B_4H_4.[9]

A recent theoretical study of the B_4H_4 molecule using RCCSD(T) method with cc-pVTZ and cc-pVQZ basis sets confirmed that the structure C_s (I) is most stable, whereas the T_d isomer is 6 kcal/mol above C_s (I) and another planar structure C_s (III) is about 13 kcal/mol above the C_s (I) isomer. Therefore, based on our calculations using DFT/ B3LYP method with 6-311+G** basis set finding that, the tetrahedral structure is the propriate isomer for B_4H_4 molecule, and the T_d isomer is 55.5 kcal/mol above C_s (I) which mean that the tetrahedral is the most stable structure for the B_4H_4 as shown in Tables 13 and 14. Therefore, as seen in Table 15, based on our calculations using the DFT/ B3LYP method with the 6-311+G** basis set, the tetrahedral structure is the propriate isomer for B_4H_4 molecule, and the T_d isomer is 55.5 kcal/mol above C_s (I) which mean that the tetrahedral is the most stable structure for the B_4H_4 .

Table 13. Calculated Energies (Hartree) of the (C_s)I , (T_d)II and (C_s)III Geometry, for B_4H_4 the Molecules at B3LYP/DFT Theory with Various Basis Sets

Basis Set		**6-31G***	**6-311G***	**6-311+G****
B_4H_4	(C_s) I	-101.61583	-101.63786	-101.64612
	(T_d) II	-101.71280	-101.72803	-101.73470
	(C_s) III	-101.58698	-101.60755	-101.61637

Table 14. The Energy Differences ΔE (kcal/mol) between (C_s)I , (T_d)II and (C_s)III Geometries

Basis Set	**ΔE**	**B_4H_4**
6-311+G*	$E((C_s)I - E(T_d)$ II (kcal/mol)	55.5
	$E((C_s)III - E(C_s)$II (kcal/mol)	18.6

Table 15. Comparison between Our Results and Papakondylis and Mavridis Results

Molecule	**Structure**	**Method/Basis Set**	
		RCCSD(T)/cc-pVTZ(5)	DFT /6-311+G**
$\mathbf{B_4H_4}$	(C_s) I	-101.45481	-101.55141
	(T_d) II	-101.44675	-101.73470
$\boldsymbol{E((C_s)I - E(T_d)}$ **II (kcal/mol)**		6.5	55.5

It is very clear from the Table 16 that the bond lengths of the same compound of the same isomers does not show any dependence on the chosen level of theory when the 6-311+G** basis sets is used. The B-B bond length of the T_d isomers of all compounds are 1.686 Å at all three levels, which is comparable to the experimentally determined bond length of 1.70 Å in B_4Cl_4 [6] and recent high level calculations of 1.685 Å.[8] The B-B bond length of the planar D_{4h} isomer is 1.726 Å or 1.727 Å, which is ~2 Å longer than the same bond of the T_d isomer. The B-X bond length in the D_{4h} isomers increase as the size of the X atom increase, i.e. the bond length is B-H< B-F< B-Cl< B-Br< B-I. The bond length trend in the T_d isomers is similar except the B-Br and B-I bond length is the same. This is somewhat unexpected, since an early study calculated the B-I bond length in the T_d isomer to be longer than the B-Br bond length[15] and that is what expected by intuition. The calculated B-H bond length is 1.181 Å which is similar to 1.185 Å calculated at the CCSD(T)/cc-pVQZ level.[8] Further discussions and the results on the B_4Cl_4 would be discussed in section 3.3, where our calculations to the experimental observations were compared.

Table 16. Calculated Energies (Hartree) of the D_{4h} and T_d Geometry, for $t-Bu_4B_4$ the Molecules at B3LYP/DFT Theory with Various Basis Sets

Basis Set	**6-31G***	**6-311G***	**6-311+G****
$\boldsymbol{t-Bu_4B_4\ (D_{4h})}$	-730.54797	-730.69499	-730.74735
$\boldsymbol{t-Bu_4B_4\ (T_d)}$	-730.76872	-730.91288	-730.96251
$\boldsymbol{\Delta E}$	138.52062	136.72597	135.01290

The B-B and B-X (X=H, F, Cl, Br, I) bond lengths calculated using the largest basis set 6-311+G** at the HF, MP2, and B3LYP/DFT levels are listed in the Table 17.

Table 17. Calculated B-B and B-X (X=H, F, Cl, Br, I) Bond Lengths Using the 6-311+G** Basis Set at the HF, MP2, and B3LYP/DFT Levels

			Bond length (Å)		
Molecule	**Structure**	**Bond**	HF level	MP2 level	DFT level
$\mathbf{B_4H_4}$	D_{4h}	B-B	1.726	1.726	1.726
		B-H	1.172	1.172	1.172
	T_d	B-B	1.686	1.686	1.686
		B-H	1.181	1.181	1.181
$\mathbf{B_4F_4}$	$D_{4\mathrm{h}}$	B-B	1.726	1.726	1.726
		B-F	1.323	1.323	1.323
	$\mathrm{T_d}$	B-B	1.686	1.686	1.686
		B-F	1.323	1.323	1.323
$\mathbf{B_4Cl_4}$	$D_{4\mathrm{h}}$	B-B	1.727	1.727	1.727
		B-CI	1.700	1.700	1.700
	$\mathrm{T_d}$	B-B	1.686	1.686	1.686
		B-CI	1.742	1.742	1.742

Continued

Molecule	Structure	Bond	Bond length (Å)		
			HF level	MP2 level	DFT level
B_4Br_4	D_{4h}	B-B	1.726	1.727	1.726
		B-Br	1.769	1.769	1.769
	T_d	B-B	1.686	1.686	1.686
		B-Br	2.100	2.100	2.100
B_4I_4	D_{4h}	B-B	1.727	1.727	1.727
		B-I	2.018	2.018	2.018
	T_d	B-B	1.686	1.686	1.686
		B-I	2.100	2.100	2.100

The harmonic vibrational spectra are shown in Tables 18 and 19 and Figures 9 and 10.

Table 18. Frequencies of T_d Isomer of the B_4X_4 Molecules

Molecule	Theory cm^{-1}	Experimental cm^{-1}
B_4H_4	2695	-
B_4F_4	1300	-
B_4Cl_4	1000	1010
B_4Br_4	800	-
B_4I_4	939	-

Table 19. Frequencies of T_d Isomer of the $B_4Br_nCl_m$ Molecules

Molecule	**Theory Cm^{-1}**	**Experimental Cm^{-1}**
B_4Br_3Cl	1001	-
$B_4Br_2Cl_2$	1000	-
B_4BrCl_3	995	-

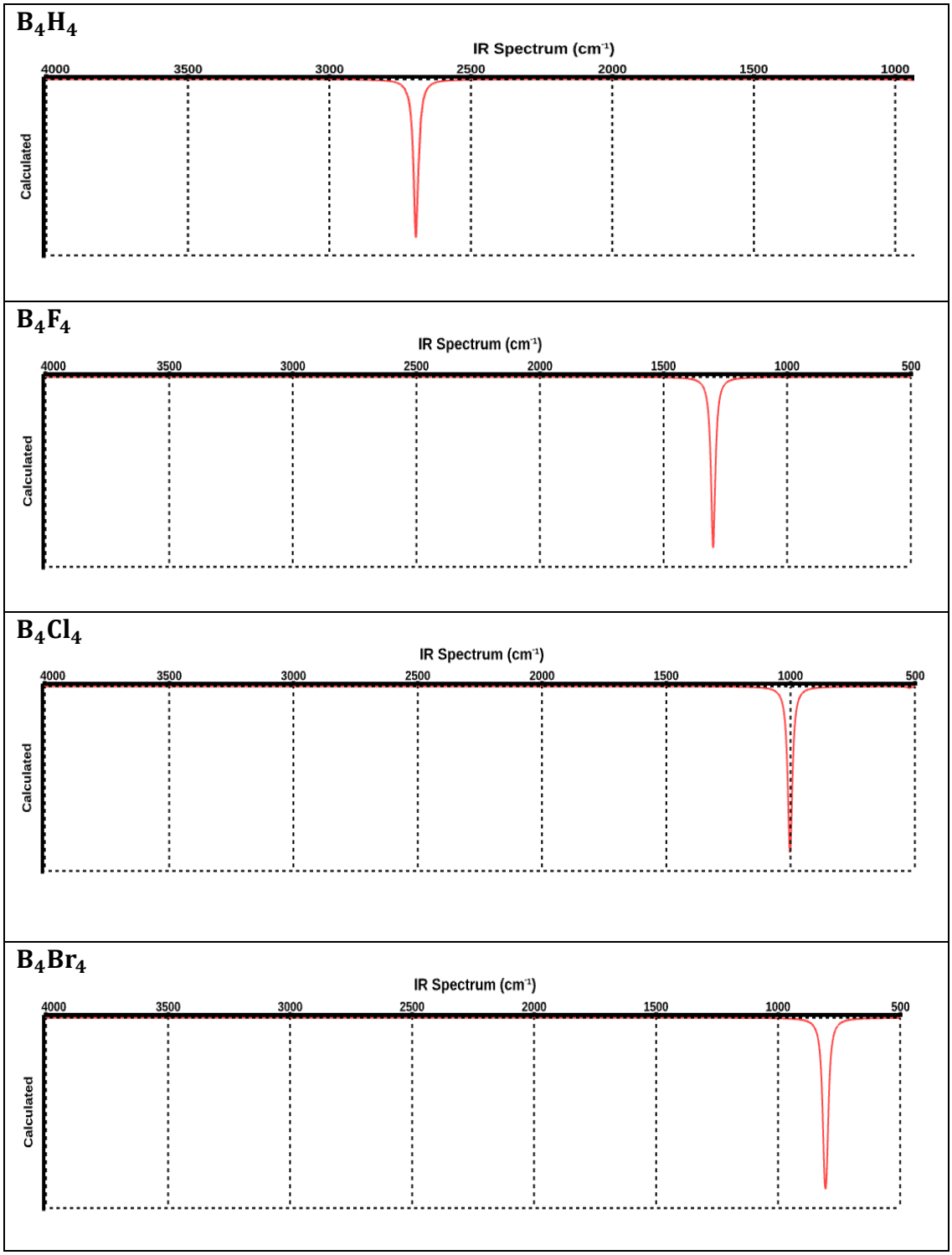

Figure 9. IR spectra of T_d isomer of the B_4X_4 molecules.

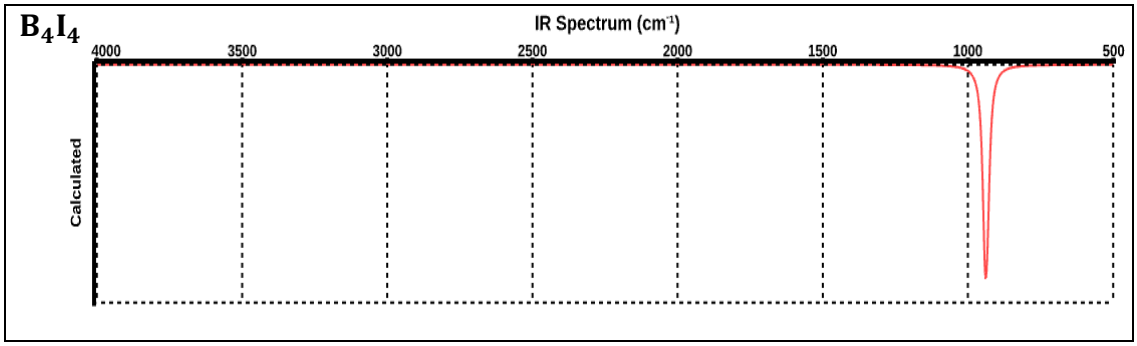

Figure 9. *Continued*

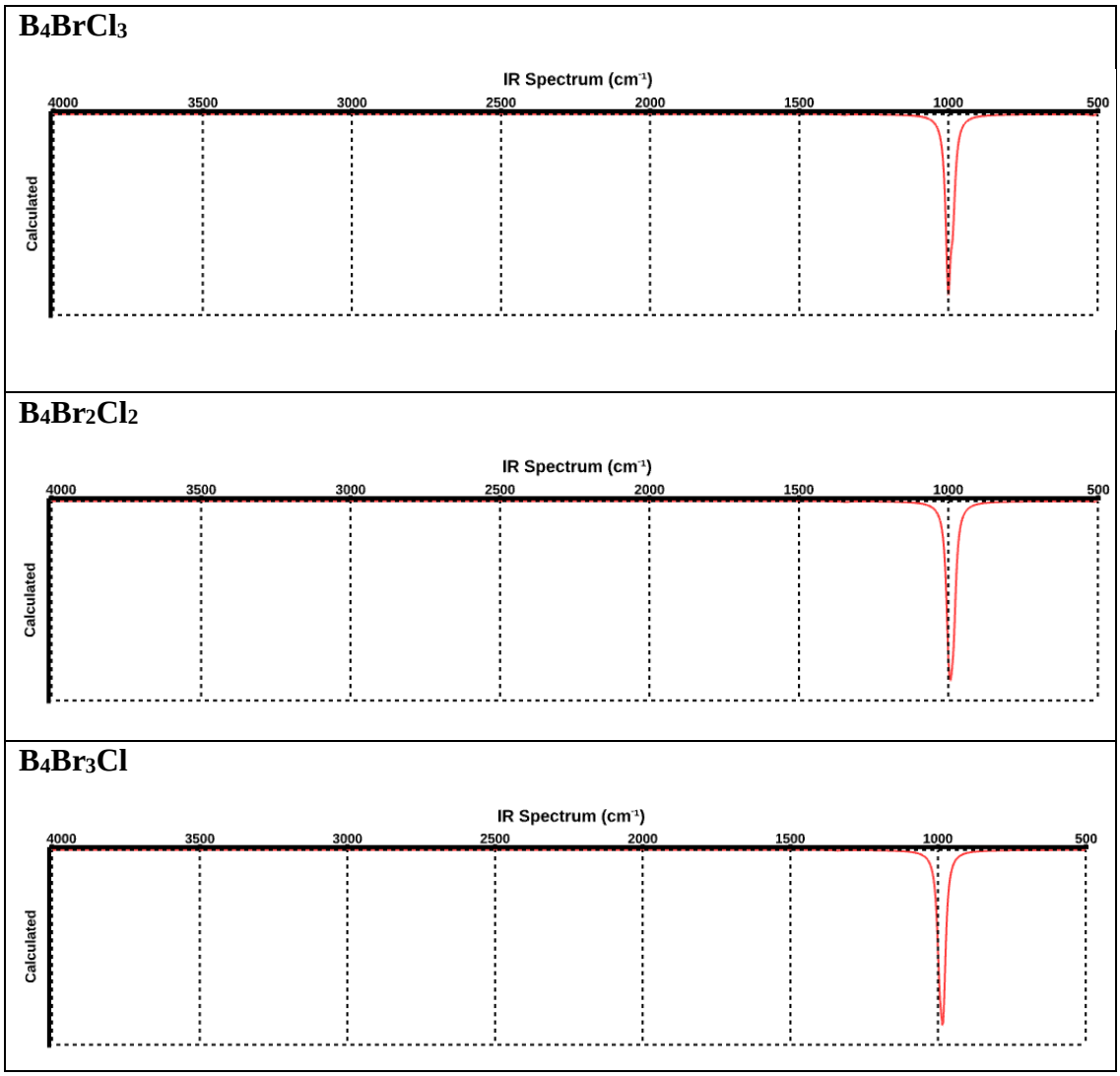

Figure 10. IR spectra of T_d isomer of the $B_4Br_nCl_m$ molecules.

3.3 Discussions

In the previous sections, results of the calculated energy and vibrational infrared spectra of the B_4X_4 (X=H, F, Cl, Br, I) molecules and the stability of the T_d isomers with respect to the D_{4h} isomers were presented. Among the molecular species that studied B_4Cl_4 were well characterized. The B-B and B-Cl bond lengths in the T_d isomer are 1.686 Å and 1.742 Å, respectively. The B-B bond length is comparable to the bond length of 1.70 Å determined from x-ray crystal structure data[6] and previous theoretical studies.[15] The B-Cl bond length is longer than the experimental bond length of 1.69 Å[6] but consistent with a theoretical study.[15] Another experimental known data of the T_d isomer of B_4Cl_4 is the vibrational spectra where a strong absorption peak is observed at 1010 cm^{-1} in the vapor[34] and a band is observed at 968 cm^{-1} in the solid.[13] The calculated harmonic infrared spectrum is shown in Figure 11. The calculated spectra is comparable to a previous study[14] and the experimental infrared spectrum of the vapor phase.[13,34] This strong peak corresponds to the B-Cl stretch vibration which is very strong when compared to other vibrations, and thus this band is the only peak that is clearly visible in the computed and experimental infrared spectrum.

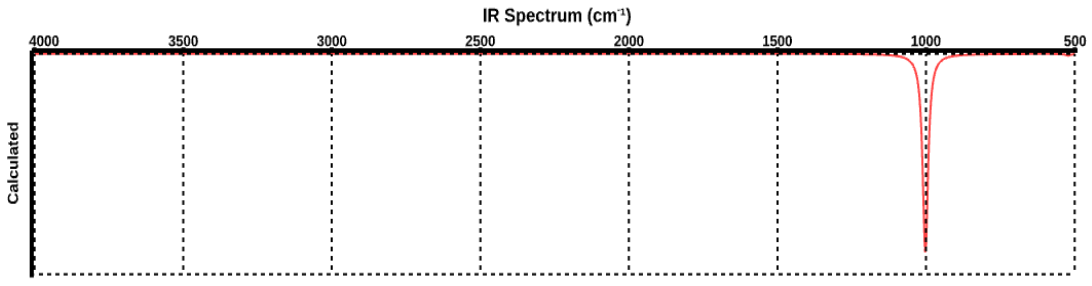

Figure 11. IR spectra of T_d isomer of the B_4Cl_4 molecule.

Additionally, ionization potential of the B_4Cl_4 molecule at the HF and DFT levels were calculated, as shown in Table 20. This was inspired by the fact that there is an experimental study on the He (I) photoelectron spectrum of B_4Cl_4that observed the ionization energy to be at 10.55 electron volt (eV).[35] There are other methods to calculate the IE very accurately albeit they are very complex and time consuming. Here, calculation of the IE based on the Koopmans' theorem which states that in closed-shell Hartree–Fock (HF) theory, the first ionization energy of a molecular system is equal to the negative of the orbital energy of the highest occupied molecular orbital (HOMO). Therefore, the calculation of the IE in using the HF method is straightforward and well-established. On the other hand, that's not so true in the case of DFT. Also, the calculated IE using the DFT methods generally underestimate the IE values.[36,37] The calculated IE energy of the B_4Cl_4 molecules using the HF method is much closer to the experimentally determined IE of 10.55 eV, and the value obtained by using the DFT functional B3LYB is smaller than the experimental value, as expected [37] shown in Table 20.

Table 20. Koopmans Ionization Potential of B_4Cl_4 Molecule

IE (eV)	Method
11.27	Hartree-Fock
8.33	Density functional theory

CHAPTER 4

CONCLUSION

Calculations performed systematic on the tetrahedral T_d and planar square D_{4h} structures of the B_4H_4 molecule, its halogen derivatives B_4X_4 (X=F, Cl, Br, I), and $B_4Br_nCl_m$ (n+m=4 and n≠0,m≠0) molecules with the objective of determining the relative stabilities of the two very symmetric isomers. The calculations carried out employing the simple and basic HF theory, its improvement, the MP2 method, and the new DFT method with the B3LYP functional, using Pople's Gaussian type basis sets 6-31G, 6-311G*, and 6-311+G*. Employment of these three different methods coupled with various basis sets enabled us to remove bias of any method and basis sets, and come to unambiguous conclusions.

First, analyses of the basis set is dependence of the energies of the T_d and D_{4h} isomers and their differences to make sure that basis sets are converged. For that purpose, the energies and relative stabilities of the isomers of the B_4H_4 molecule, the B_4Br_4, and the $B_4Br_nCl_m$ **(**n+m=4 and n≠0,m≠0) molecule series were compared. The electronic energies and their differences between the two isomers of the same molecular species only show small change when the basis set is increased from 6-311G* to 6-311+G**, confirming basis set convergence and that the 6-311+G** basis set is large enough. Thus, quantitative results from using the 6-311+G** basis set are achieved. However,

the results of the HF calculation on the B_4Cl_4 square planar structure D_{4h} shows no sign of basis set convergence, where the electronic energy decrease ~62 kcal/mol when the basis set increased from 6-311G* to 6-311+G**. The T_d isomer at the same level does converge. At HF/6-311+G** level, the T_d isomer of B_4Cl_4 is only 28 kcal/mol more stable than the planar D_{4h} structure. This is the smallest among all molecules at all levels, and it is clearly that the main reason is that correlation energy at HF level ignored for the D_{4h} isomer. Further studies employing larger basis sets at the HF level may eliminate this anomaly.

The largest basis set were used 6-311+G** which is large enough to get the conclusion. The T_d configurations of all the molecules considered here are more stable, at least by 28 kcal/mol, than D_{4h} isomers of the same molecule, at all levels of theory and basis sets. The calculated B-B bond lengths of the T_d isomers are 1.686 Å, which are comparable to previous studies, and are comparable to the experimentally determined bond length of 1.70 Å in the B_4Cl_4 molecule. The B-X bond lengths are, again, similar to previous studies but are systematically ~0.02 Å longer than the B-Cl length of 1.70 Å determined experimentally. Also, normal mode calculations on these molecules were performed, and there are no imaginary frequencies, confirming the geometry is a true minimum, not a transition state. The calculated infrared spectrum of the B_4Cl_4 molecule of the T_d structure shows a strong peak close to ~1000 cm^{-1}, similar to previous theoretical calculations, and are also comparable to the experimental spectrum that shows a broad band centered at 1010 cm^{-1}. Also, implemented simple ionization potential calculations on the B_4Cl_4 molecule and show that the HF method yields values that are

closer to the experimental one than compared to the value obtained by the DFT functional B3LYB.

REFERENCES

1. Mckee, M. L.; Lipscomb, W. N. Theoretical-Study of the Isomerization of Hypothetical B_4H_4. *Inorg. Chem*. **1981**, 20, 4148-4151.

2. Ahmed, L.; Castillo, J.; Morrison, J. A. Chemistry of Tetraboron Tetrachloride - Synthesis and Characterization of Tetraboron Tetrabromide (B_4Br_4) and Observation of B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl. *Inorg. Chem*. **1992**, 31, 1858-1860.

3. J. H. Hall, Jr.; W. N. Lipscomb. Ab-Initio Self-Consistent Field Study of Boron Halides: B_4F_4 and B_4Cl_{4-}. *Inorg. Chem*. **1974**, 13, 710 -714.

4. Swanton, D. J.; Ahlrichs, R. Electronic-Structures of the Boron Cage Molecules B_4H_4, B_4Cl_4 and B_4F_4. *Theor. Chem. Acta.* **1989**, 75, 163-172.

5. Urry, G.; Wartik, T.; Schlesinger, H. I. A New Sub-Chloride of Boron, B_4Cl_4. *J. Am. Chem. Soc*. **1952**, 74, 5809-5809.

6. Atoji, M.; Lipscomb, W. N. The Molecular Structure of B_4Cl_4. *J. Chem. Phys.***1953**, 21, 172-172.

7. Mach, P.; Hubac, I.; Mavridis, A. Ab Initio Structural Study of the B_4H_4 Molecule. Asymmetric Structure for a "Symmetric" System. *Chem. Phys. Lett.* **1994**, 226, 469-474.

8. Papakondylis, A.; Mavridis, A. The Story of the B_4H_4 Molecule Told Again. *Comput. Theor. Chem.* **2017**, 1115, 217-222.

9. Olson, J. K.; Boldyrev, A. I. Ab Initio Search for Global Minimum Structures of Neutral and Anionic B_4H_4 Clusters. *Chem. Phys.* **2011**, 379, 1-5.

10. Kleier, D. A.; Bicerano, J.; Lipscomb, W. N. Stereochemical Rigidity and Isomerization in Tetraborane(4) and Tetrafluorotetraborane(4). A Theoretical Study. *Inorg. Chem*. **1980**, 19, 216-218.

11. Lipscomb, W. N. 3-Center Bonds in Electron-Deficient Compounds - Localized Molecular-Orbital Approach. *Acc. Chem. Res.* ***1973***, 6, 257-262.

12. Morrison, J. A., Chemistry of the Polyhedral Boron Halides and the Diboron Tetrahalides. *Chem. Rev*. **1991**, 91, 35-48.

13. Brown, F. R.; Miller, F. A.; Sourisseau, C. The Vibrational Spectrum of B_4Cl_4. *Spectrochimica Acta.* **1975**, 32, 125-136.

14. Jensen, J. O., Vibrational Frequencies and Structure of B_4Cl_4: An Ab Intio Quantum Chemical Study. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. **2002**, 58, 2299-2309.

15. Lin, C.-S. L.; Liu, C.-W. J. Theoretical Study on Tetranuclear Boron Clusters: B_4X_4 (X = H, F, Cl, Br, I). *Chine. J. Chem*. **1994**, 12, 305-313.

16. Del Bene, J. E.; Alkorta, I; Elguero, J. B_4H_4 and B-4(CH_3)(4) as Unique Electron Donors in Hydrogen-Bonded and Halogen-Bonded Complexes. *J. Phys. Chem. A*. **2016**, 120, 5745-5751.

17. Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. *Mathematical Proceedings of the Cambridge Philosophical Society*. **1928**, 24, 89-110.

18. Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion. *Mathematical Proceedings of the Cambridge Philosophical Society*. **1928**, 24, 111-132.

19. Sherrill, C. David. *An Introduction to Hartree-Fock Molecular Orbital Theory*. Georgia Institute of Technology, School of Chemistry and Biochemistry: Atlanta, GA. June 2000.

20. Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev*. **1934**, 46, 618-622.

21. McGibbon, R. T.; Taube, A. G.; Donchev, A. G.; Siva, K.; Hernández, F.; Hargus, C.; Law, K.-H.; Klepeis, J. L.; Shaw, D. E. Improving the Accuracy of Møller-Plesset perturbation Theory with Neural Networks. *J. Chem. Phys*. **2017**, 147, 161725.

22. Young, D. C. *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*. John Wiley & Sons, Inc.: New York, 2002, pp 19-46.

23. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* B. **1964**, 136, 864-871.

24. Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys*. **1993**, 98, 5648-5652.

25. Burke, K.; Wagner, L. O. DFT in a Nutshell. *Int. J. Quant. Chem*. **2013**, 113, 96-101.

26. McKechnie, S.; Booth, G. H.; Cohen, A. J.; Cole, J. M. On the Accuracy of Density Functional Theory and Wave Function Methods for Calculating Vertical Ionization Energies. *J. Chem. Phys*. **2015**, 142, 194114.

27. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B*. **1988**, 37, 785-789.

28. Wavefunction, Inc., The Spartan16 Software, Irvine, CA. http:// www.wave fun.com.

29. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys*. **1980**, 72, 650-654.

30. Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys*. **1972**, 56, 2257-2261.

31. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-Row Elements. *J. Chem. Phys*. **1982**, 77, 3654-3665.

32. Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-Consistent Molecular Orbital Methods 25. Supplementary Functions for Gaussian Basis Sets. *J. Chem. Phys*. **1984**, 80, 3265-3269.

33. Atkins, P. W.; Friedman, R. S. *Molecular Quantum Mechanics*, 5th ed.; Oxford University Press: USA, 2010; p 592.

34. Urry, G.; Garrett, A. G.; Schlesinger, H. I. The Chemistry of the Boron Subhalides. I. Some Properties of Tetraboron Tetrachloride, B_4Cl_4. *Inorg. Chem*. **1963**, 2, 396-400.

35. Lebreton, P. R.; Urano, S.; Shahbaz, M.; Emery, S. L.; Morrison, J. A. He-I Photoelectron-Spectra, Valence Electronic-Structure, and Back Bonding in the Deltahedral Boron Chlorides, B_4Cl_4, B_8Cl_8, and B_9Cl_9. *J. Am. Chem. Soc.* **1986**, 108, 3937-3946.

36. Politzer, P.; Abu-Awwad, F. A comparative analysis of Hartree-Fock and Kohn-Sham Orbital Energies. *Theor. Chem. Acc.* **1998**, 99, 83-87.

37. Tsuneda, T.; Song, J.-W.; Suzuki, S.; Hirao, K. On Koopmans' Theorem in Density Functional Theory. *J. Chem. Phys.* **2010**, 133, 174101.